Lead isotopes and pollution history

K J R Rosman & W Chisholm

Deptartment of Applied Physics, Curtin University of Technology, Bentley, WA 6102

Abstract

Lead is one of the seven metals of antiquity and its production is highly correlated with the development of industrial civilisations. This paper reviews the awakening during the 1960s of modern humans to the environmental and health problems associated with the use of lead. The difficulty of measuring lead received little attention until the mid 1960s when it was realised by geochemist C C Patterson and colleagues at the California Institute of Technology that the world was immersed in a lead mist. This awareness prompted analysts to develop clean-air laboratories and to take special precautions when collecting and analysing samples for lead. Thermal ionisation mass spectrometry has played a vitally important role in this process by offering a high-sensitivity detection tool, and the means of uniquely identifying artifact lead contamination through its isotopes. Today this tool is being used to identify the origin of lead in natural archives such as the Greenland and Antarctic ice sheets. This paper discusses the development of this field.

Introduction

Significant lead production began about 5000 years ago with the discovery of cupellation. Lead sulphide ores were smelted to produce lead-silver alloy which yielded metallic silver on oxidation. Smelting led to local pollution but also released lead to the atmosphere. However it was only during Greek and Roman times, about 2500 years ago, that atmospheric pollution from this source reached levels where evidence of the fossil remnants could be detected in Greenland ice (Hong *et al.* 1994).

Lead has been associated with human health problems since antiquity and may have contributed to the fall of Rome (Nriagu 1983). Its toxic effects on humans are now well understood and childhood lead poisoning is of great concern (Mushak *et al.* 1989; McMichael *et al.* 1988). Lead is a non-degradable poison and has been produced at an increasing rate during the twentieth century. Vast quantities have been used in paint and as an anti-knock agent in petrol, creating a problem of global dimensions which this and future generations must resolve (Rabin 1989; Nriagu 1990; Needleman 1991).

Although lead has created tremendous problems for mankind, the formation of its isotopes by radioactive decay allowed the first accurate determination of the Earth's age (Patterson 1956). The array of isotopic abundances found in crustal rock and lead ore has been the key to the identification of anthropogenic lead in ancient ice and is the basis of a method for tracing lead and associated pollution around the globe. The two primary instruments used for these studies are the mass spectrometer and the ultra-clean sample preparation laboratory. The last three decades have witnessed dramatic improvements in mass spectrometer sensitivity (>10⁶ for some elements) through the development of new ionisation methods (Cameron *et al.* 1969; Rosman *et al.*

1984) and vastly improved techniques for sampling and preparing small samples for analysis (Patterson & Settle 1976). These techniques have now been refined to the point where the isotopic composition of lead in remote snow and ice can be reliably measured (Rosman *et al.* 1993).

This paper briefly reviews the motivation for constructing a lead pollution history for the global atmosphere and shows how the measurement of lead isotope abundances complements concentration measurements by providing a method to identify the source of pollution.

Pollution History

A variety of natural archives have been used to construct pollution histories; these include river, lake and marine sediments, peat bogs, glaciers, the polar ice caps and tree rings. In these archives, the anthropogenic species are trapped in layers and remain essentially isolated from each other. A pollution history can be established by measuring the species and the corresponding deposition age. Time scales for these archives vary from years to millennia.

The impetus for constructing a pollution history of lead for the Northern Hemisphere came from Clair C. Patterson of the California Institute of Technology (CIT), who, together with colleagues T Chow and M Tatsumoto, found that industrial lead was having a profound influence on the lead content of the oceans and atmosphere. Although the measurements of lead in sea water in their earlier studies were later found to be in error by a large amount due to contamination problems, their conclusions were correct. Following the publication of a paper entitled *Contaminated and Natural Environments of Man* (Patterson 1965), Patterson directed his research effort towards understanding the impact that anthropogenic lead was having on the biogeochemical cycle of lead. This paper created much public interest, controversy amongst scientists, and corporate concern. Differences of opinion

between scientists often arose from a lack of awareness of the real difficulties of analysing lead at low concentration, either in the field or in the laboratory. Ignorance of these problems still persists today.

Patterson began his 1965 paper: *"A prevailing belief is that industrial and natural sources contribute more or less equal amounts of lead to the body burdens of the general population. ......".* He proceeded to demonstrate with geochemical arguments, using the relatively poor data of the time, that the average resident of the U.S.A. had a body burden for lead one hundred times above natural levels. Questions raised in his paper were the subject of CIT research for the following three decades. One recommendation arising from his study was the need to establish "natural" lead levels as opposed to the "typical" levels found in modern environments, and so a lead pollution history for the Northern Hemisphere extending back in time almost three millennia was constructed.

The concentration of lead was measured in dated layers of Greenland snow and ice extending from 1965 AD back to 800 BC (Murozumi *et al.* 1969). This was a remarkable accomplishment for its time. The time series covering the period 1753-1965 was established by analysing preserved layers of snow and ice taken from the walls of trenches and shafts at Camp Century (77°10'N, 61°08'W, elevation 1.87 km) and a site 80 km away in north west Greenland. The ice sample dated 800 BC was collected from Camp Tuto (76°25'N, 68°20'W). These measurements initially caused controversy among geochemists because they raised doubts about the quality of published data on polar snow, but the results were eventually confirmed and extended (Ng & Patterson,1981; Boutron *et al.* 1991; Candelone *et al.* 1995). Figure 1 summarises the results of these measurements.
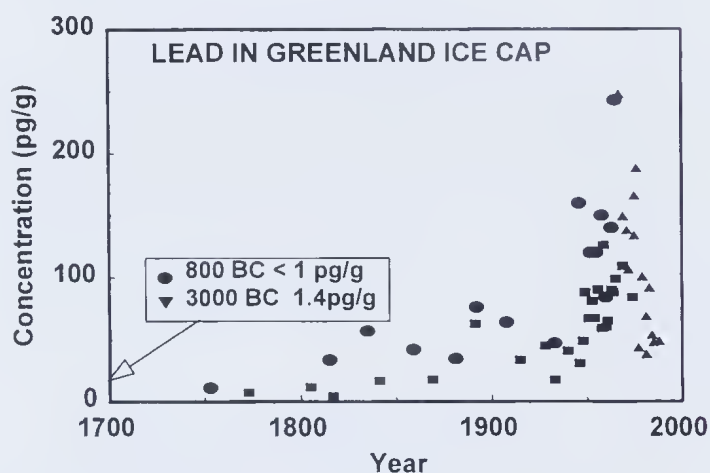

Figure 1. Changes in the concentration of lead in Greenland snow and ice dating from 3000 BC to the present. Adapted from Murozumi *et al.* (1965) - ellipses; Boutron *et al.* (1991) - triangles; Candelone *et al.* 1995 - squares, Ng & Patterson 1981 - inverted triangle.

To identify the source of lead emissions to the atmosphere, it is necessary to tag each source in some way. Isotopic fingerprinting can be very effectively used for lead when there are natural variations between sources. Early workers were well aware of the potential of this technique and were successful in identifying sources of

local pollution (Chow & Johnstone 1965), but only recently has it been possible to use the technique to investigate sources of atmospheric pollution on a hemispheric scale (Rosman *et al.* 1993).

Lead Isotopes

Lead has four naturally occurring stable isotopes, ^{204}Pb which was only formed by nucleosynthesis and three others which are also end products of radioactive decay chains: $^{238}U \Rightarrow {}^{206}Pb$, $^{235}U \Rightarrow {}^{207}Pb$ and $^{230}Th \Rightarrow {}^{208}Pb$ with halflives $4.5 \ 10^9$, $0.71 \ 10^9$ and $14 \ 10^9$ years respectively. Consequently, lead isotopes in rocks and minerals of different chemical composition and in lead ore bodies of different ages, which are the source of industrial lead, display large abundance variations that can easily be measured in a mass spectrometer.

Soddy, who introduced the term "isotope", suggested in 1913 that because lead was formed by the radioactive decay of uranium and thorium, then minerals rich in these elements would have lower and higher atomic weights, respectively, than common lead. This prediction was confirmed within a year by number of reports (Table 1) and provided early confirmation of the existence of isotopes.

Table 1

Early evidence of natural variations in the abundance of lead isotopes (from Aston 1942). Minerals: [a]Ceylon thorite, [b]Carnotite, [c]Norwegian cleveite, [d] Norwegian thorite.

| | atomic weight | | |
Investigators	high U	common Pb	high Th
		≈207.19	
Soddy & Hyman (1914)			207.694[a]
Curie (1914)	206.36[b]		
Richards & Lembert (1914)	206.08[c]		

Lead Isotopes in the Environment

Interest in the use of isotope abundance variations for tracing sources of industrial lead began in the early 1960s (Tatsumoto & Patterson 1963; Chow & Johnstone 1965) and evolved from earlier geochemical studies by Chow, Patterson and Tasumoto who had all been associated with the same CIT laboratory. Since this time, lead isotopes have been used as natural tracers on a number of occasions, but the number of studies have been relatively few considering the potential of this approach for solving environmental problems. One particularly significant early study was that by Chow *et al.* (1975) who assessed lead isotopic abundance variations in aerosols, gasoline and soil in various countries by spot sampling during the period 1964 - 1974. They also monitored temporal variation in San Diego (USA) aerosols over the same period which revealed a clear trend in isotopic composition.

Since this time, pollution histories that include isotopic data have been published for a range of different natural archives, including for example river sediments (Shirahata *et al.* 1980), lake sediments (Ritsen *et al.* 1994) marine sediments (Hirao *et al.* 1986), coral (Shen & Boyle 1987) and snow (Rosman *et al.* 1993).

Isotopic Fingerprinting in Snow and Ice

Pollution histories based on lead in recent snow and ice are relatively simple to interpret because the natural background contribution is generally negligible. Murozumi *et al.* (1969) showed that the background (pre-Roman) concentration of lead in remote Greenland snow and ice was only $\approx$1pg g^{-1}, which was cleaner than the water found in most analytical chemistry laboratories.

Reliable isotope abundance measurements of lead in pre-industrial ice demand that the following be available:

1. ultra-clean procedures for the acquisition and storage of field samples;

2. ultra-clean decontamination procedures;

3. ultra-clean sample storage;

4. ultra-clean sample processing for mass spectrometry;

5. sensitive high precision mass spectrometry.

Murozumi *et al.* (1969) showed incredible skill in measuring pg g^{-1} concentrations, of lead in Greenland ice. To minimise the contributions from artifact contamination they collected 19 kg or 50 kg size blocks of ice. Thirteen years later, Ng & Patterson (1981) required only 100-200 g samples to confirm the results of the earlier study. The corresponding laboratory blanks for these two studies were $\approx$100 ng and 160 pg, the later amounting to $\approx$30% of the cleanest sample analysed.

The size of samples typically used today for isotopic analyses vary from 1-50 g depending on their lead concentration, while the total laboratory processing blank has improved steadily to $\approx$ 3 pg in 1993 (Rosman *et al.* 1993) and finally $\approx$ 0.5 pg today (author's laboratory). The improvement in the blank/sample ratio in the 1990s arose from the realisation that snow collected at remote locations is relatively free of impurities and consequently processing can be kept to a minimum, and should ideally be avoided. Whereas earlier studies (Murozumi *et al.* 1969; Ng and Patterson 1981; Boutron & Patterson 1986) using mass spectrometers for lead concentration measurements attempted to purify the lead using chemical methods such as ion exchange or solvent extraction, current practice is to concentrate the sample by evaporation in an ultraclean environment (Rosman *et al.* 1993, 1994a,b; Chisholm *et al.* 1995).

The capability of current methods can best be illustrated with measurements on the purest laboratory water. Figure 2 shows measurements of lead in three different masses. The concentration of lead in the water is calculated from the gradient of the line through the points (0.013 pg g^{-1}) , and the procedural blank is determined from the intercept (0.47 pg). In practice, ice samples are normally measured only once or twice, procedural blanks are checked by monitoring critical reagents, and the effectiveness of the beaker cleaning procedures and the quality of the laboratory water are checked by evaporating equivalent volumes of ultra-pure water in beakers prior to using them for a sample.

Lead concentrations are measured by isotope dilution mass spectrometry (IDMS) with a minor variation. A known amount of ^{205}Pb-enriched tracer (half-life 1.5 10^7) is mixed with the sample prior to analysis. The quantity
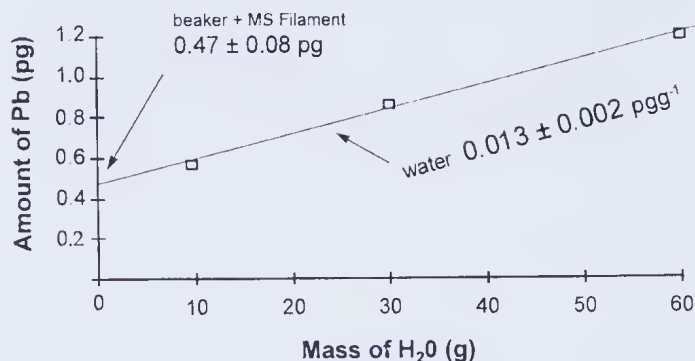
LABORATORY WATER

Figure 2. The concentration of lead in ultra-pure laboratory water. The gradient of the line yields the lead concentration and the intercept gives the analytical blank.

of natural lead can be determined from the measurement of the mixed lead mass spectrum. Because ^{205}Pb does not occur naturally, the use of this tracer permits the isotopic composition to be determined in the same measurement.

A vital step in the chain of procedures needed for a reliable measurement of lead in ice is the decontamination process. The purpose is to mechanically remove contaminated ice, layer by layer, ideally resulting in a central core of uncontaminated ice. Each layer is analysed to confirm the effectiveness of the procedure. (Ng & Patterson 1981; Candelone *et al.* 1994). Figure 3 shows the concentration profile for a section of the Vostok ice core drilled in Antarctica by a team from the former Soviet Union (Chisholm *et al.* 1995). In this case, however, the contaminant lead penetrated the central core and only an upper limit of concentration could be given. The criterion for an uncontaminated central core is that the concentration must reach a constant value. This approach was developed by Ng & Patterson (1981) and is still the most reliable method of validating the purity of the central sample. However the advent of isotope abundance measurements added another dimension to
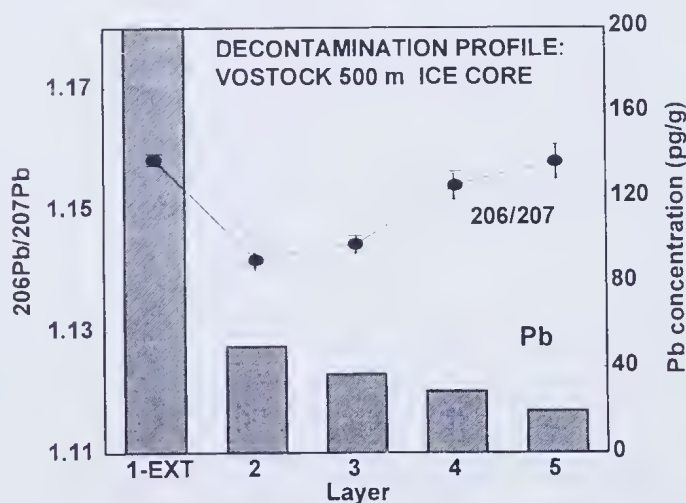

Figure 3. Lead concentration and isotopic ratio profile across a Vostok ice core. The sample was taken from a depth of 500 m (26.2 ka BP) using a thermally drilled hole with kerosene as the retaining fluid.

this process by allowing different sources of contamination to be resolved. In Figure 3, the outer layers show an initial decrease in isotopic ratio then an increase, but never reach a constant value. This pattern suggests that there are two sources of artifact lead in addition to the natural component. The lead concentration is highest on the outside and also continues to change as the centre of the core is approached, confirming that artifact lead is still present. This analysis can only yield an upper limit of concentration and a lower limit of isotopic ratio.

Lead Pollution History of the Northern Hemisphere

The Greenland ice cap penetrates the troposphere and rises to an altitude of ~ 3.23 km at Summit (72°35'N, 37°38'W) near the centre of the island. Aerosols are scavenged by falling snow which accumulates on the ice cap and is eventually converted to ice when it reaches a depth of about 80 m. The analysis of snow and ice from various depths provides a record of the pollution history of the Northern Hemisphere. The analysis of pre-Roman ice is essential for a correct interpretation of post-industrial changes while much older ice provides useful information on early climatic conditions.

The oldest ice collected to date ($\approx$250 ka) was retrieved recently by the European GRIP (Greenland Ice Core Program) and the United States GISP (Greenland Ice Sheet Program) teams who drilled $\approx$3 km to the basement at two sites near Summit (Dansgaard *et al.* 1993; Grootes *et al.* 1993). Shallower sampling in the same area has also provided interesting complementary information. For instance, an 11 m snow core taken with a polycarbonate hand-operated auger (to minimise contamination) and a 70 m electromechanically drilled core were both taken during the recent European "Eurocore" program (Boutron *et al.* 1991; Candelone *et al.* 1995). Boyle *et al.* (1995) also report lead concentration measurements to a depth of 6 m at Summit. In the latter study, two series of samples were taken - one from the walls of a snow pit and the other with a solar powered electric coring rig.

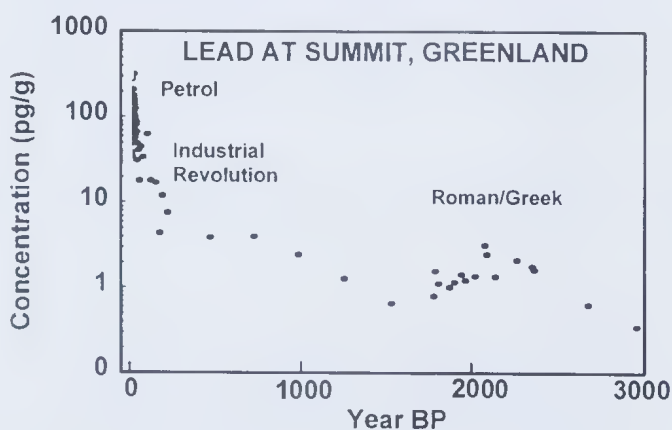The analyses of these samples has allowed a lead pollution history of the Northern Hemisphere to be constructed covering one full glacial cycle (Boutron *et al.* 1991; Candelone *et al.* 1995; Hong *et al.* 1994), and has confirmed the earlier measurements by Murozumi *et al.* (1969). Figure 4 summarises the results of these measurements and shows the periods of history when lead pollution was prominent.

Only during the 1990s have reliable lead isotope abundance data in Greenland and Antarctic snow and ice become available. When Boutron *et al.* (1991) analysed an 11 m snow core from Summit they attributed the decreasing concentration of Pb during the 1980s to the rapid reduction in the use of leaded gasoline in the United States. The analyses of lead isotopes in these samples by Rosman et al (1993, 1994a) confirmed this hypothesis. The variation of the ^{206}Pb/^{207}Pb isotope ratio found in these samples is shown in Figure 5 with the signatures of lead used in United States and Eurasian gasoline superimposed. From these data, Rosman *et al.* (1994a,b) computed the concentrations of US and Eurasian lead in Greenland snow (Figure 6). The results were in excellent agreement with the known pattern of leaded petrol consumption.
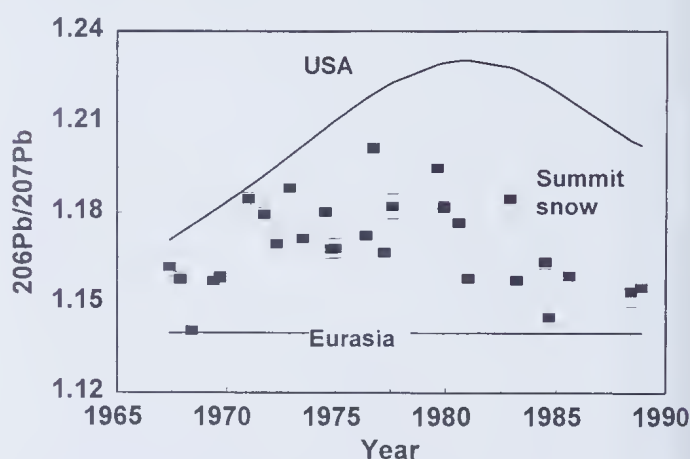
Figure 5. The ^{206}Pb/^{207}Pb isotopic ratios in snow from Summit, central Greenland (Rosman *et al.* 1993). The USA and Eurasian isotopic signatures taken from the literature are shown (Adapted from Rosman *et al.* 1994a).
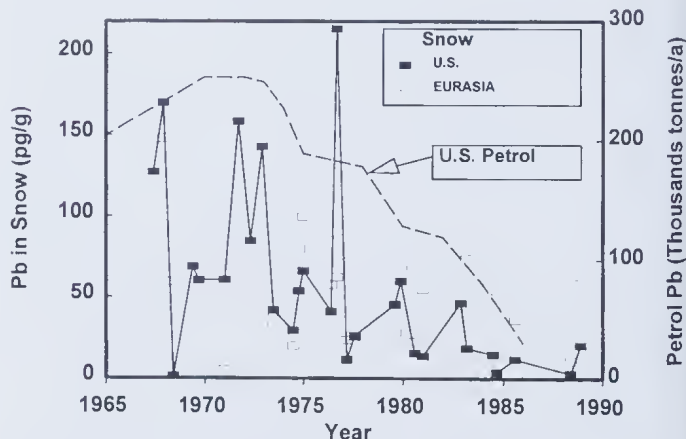
Figure 4. Recent measurements of the lead concentration in Greenland ice extending back to 3000 BP. Events causing significant changes in lead emissions to the atmosphere are identified, namely the introduction of leaded petrol, the Industrial Revolution, and the Greek/ Roman civilisations. Data from Boutron *et al.* (1991), Candelone *et al.* (1995) and Hong *et al.* (1995).

Figure 6. Comparison of USA and Eurasian lead in Summit snow with lead emissions from USA petrol. The concentrations were calculated from the isotopic ratios shown in Figure 5 and the total concentration of lead in the snow (Adapted from Rosman *et al.* 1994a).

Hong *et al.* (1994) reported relatively high lead concentrations in two thousand year old ice from the GRIP ice core and attributed this to pollution of the atmosphere by industrial emissions caused by the Greek and Roman civilisations. Preliminary measurements on these samples now show a significant decrease in the ^{206}Pb/^{207}Pb ratio which correlates with the enhanced lead concentration. These isotopic measurements are highly significant because they provide definitive evidence that this lead had an anthropogenic origin (Rosman *et al.*, 1995).

Lead Pollution History of the Southern Hemisphere

The Antarctic ice sheet is ideally located to record pollution in the Southern Hemisphere but the transfer of pollutants to Antarctica from populated regions is less direct than it is for Greenland. Although both landmasses extend to $\approx 60°$ latitude, Greenland is flanked by continents which extend into the Arctic whereas Antarctica is isolated from the influence of other land masses by the circumpolar convergence, which is a extremely effective barrier. Even so, Antarctica is highly polluted with anthropogenic lead although the concentrations in surface snow are one to two orders of magnitude lower than in Greenland.

Because the concentrations are very low, few reliable lead data for Antarctic snow and ice are available. Using elaborate sample collection and decontamination procedures, Boutron & Patterson (1987) measured concentrations as low as 2.3 pg g^{-1} in snow 433 km from the coast near the French base of Dumont d'Urville. This snow fell near the end of 1982 and during 1983. Geochemical arguments were used to show that $\approx 80\%$ of this lead was anthropogenic. Recent isotopic abundance measurements on the same sample gave a ^{206}Pb/^{207}Pb ratio of 1.16 compared with 1.07 for petrol and 1.25 for natural dust which indicated that at least 50% of the lead was anthropogenic (Rosman *et al.* 1994b).

Lead histories for Antarctica are limited to a few reliable studies. Even so, only selected reports will be identified here. Recently Wolff & Suttie (1994) produced a time series from the 1920s and observed concentrations of ≈ 2.5 pg g^{-1} for 1920-1960 increasing to a peak between 1978-1980 of ≈ 10 pg g^{-1} then falling back to ≈ 5 pg g^{-1} by the mid 1980s. Boutron & Patterson (1986, 1987) reported time series for ancient ice which they obtained from a thermally drilled core from Dome C (77°39'S, 124°10'E and elevation 3.24 km; samples to 27 Ka BP) and an electromechanically drilled core from Vostok (78°28'S, 106°48'E and elevation 3.49 km; samples to 155 ka BP). Concentrations at Dome C were as low as 0.3 pg g^{-1} during the Holocene (back to 13 ka BP) but they peaked at 29 pg g^{-1} during the coldest period of the last ice age (≈ 21 ka BP). Corresponding concentrations for the earlier glacial cycle at Vostok were 2.4 pg g^{-1} and 19.8 pg g^{-1} respectively.

Only three measurements of lead isotopes in ancient Antarctic ice have been reported. These include two Dome C ice core samples dated at 7.5 ka BP and 14 ka BP, which gave ^{206}Pb/^{207}Pb ratios of 1.25 and 1.20 respectively (Rosman *et al.* 1994b; Chisholm *et al.* 1995).

The Future of Lead Isotopes and Pollution History

Lead isotopes offer a powerful tool for identifying sources of pollution and they are a valuable complement to concentration measurements.

Measurements on recent Greenland snow have already demonstrated how leaded petrol emissions from the USA and Eurasia can be identified and their relative contributions assessed. Work is currently in progress that will extend the lead isotope record for the Northern Hemisphere back to Roman times and beyond. These data will provide new and interesting information regarding the source of the lead emissions in earlier times.

Measurements on deep cores both from Greenland and Antarctica will also provide additional information on the climatic conditions which existed on Earth during the recent glacial cycles. The concentration of the lead in the ice and its isotopic composition will reflect the atmospheric conditions and the geographical origin of the dust containing the lead.

Very few isotope abundance measurements have been made in Antarctica but the technology is now available for the measurements of existing cores to proceed. Detailed measurements at high depth resolution will be needed to identify seasonal influences and to follow the development of industry in the Southern Hemisphere. It is anticipated that high resolution cores (high deposition rates) drilled in the Law Dome by Australian teams will provide samples suitable for such studies.

The origin of the dust reaching Antarctica is not known at present. Evidence from isotopic (Grousset *et al.* 1992 ; Rosman *et al.* 1994) and geochemical (Delmas & Petit 1994) studies are in agreement but conflict with predictions from global circulation models (Joussaume 1993). Isotopic studies on snow and ice coupled with atmospheric monitoring of present day aerosols will help to resolve this problem.

The skills required for the collection, decontamination, elemental and isotopic analysis of the cleanest snow and ice samples are not limited to one laboratory. This is an activity which continues to benefit greatly by international scientific collaboration.

References

Aston F W 1942 Mass Spectra and Isotopes. (2nd ed.). Edward Arnold London.

Boutron C F & Patterson C C 1986 Lead concentration changes in Antarctic ice during the Wisconsin/Holocene transition. Nature 323:222-225.

Boutron C F & Patterson C C 1987 Relative levels of natural and anthropogenic Pb in recent Antarctic snow. Journal of Geophysical Research 92:8454-8464.

Boutron C F, Gorlach U, Candelone J-P, Bolshov M A & Delmas R J 1991 Decrease in anthropogenic Pb, Cd and Zn in Greenland snows since the late 1960s. Nature 353: 153-156

Boyle E A, Sherrell R M & Bacon M P 1994 Lead variability in the western North Atlantie Ocean and central Greenland ice: Implications for the search for decadal trends in anthropogenic emissions. Geochimica et Cosmochimica Acta 58:3227-3238.

Cameron A E, Smith D H & Walker R L 1969 Mass spectrometry of nanogram-size samples of lead. Analytical Chemistry 41:525-526.

Candelone J-P, Hong S & Boutron C F 1994 An improved method for decontaminating polar snow or ice cores for heavy metal analysis. Analytica Chimica Acta 299:9-16.

Candelone J-P, Hong S, Pellone C & Boutron C F 1995 Post-Industrial Revolution changes in large scale atmospheric pollution of the Northern Hemisphere for heavy metals as documented in central Greenland snow and ice. Journal of Geophysical Research 100, 16,605-16,616.

Chisholm W, Rosman K J R, Boutron C F, Candelone J P & Hong S 1995 The determination of lead isotopic ratios in Greenland and Antarctic snow and ice with picogram per gram concentrations. Analytica Chimica Acta 311:141-151.

Chow T J & Johnstone M S 1965 Lead isotopes in gasoline and aerosols of Los Angeles basin, California. Science 147:502-503.

Chow, T J, Snyder C B & Earl J L 1975 Isotope ratios of Pb as pollutant source indicators. United Nations FAO and International Atomic Energy Association Symposium, Vienna Austria. (IAEA-SM-191/4) Proceedings, pp. 95-108.

Curie M M 1913 Sur les ecarts de poids atomiques obtenus avec le plomb provenant de divers mineraux. Comptes Rendus. Academie des Sciences. 1676-1679.

Dansgaard W, Johnsen S J, Clausen H B, Dahl-Jensen D, Gundesstrup N S, Hammer C U, Hvidberg C S, Steffensen J P, Sveinbjornsdottir A E, Jouzel J & Bond G 1993 Evidence for general instability of past climate from a 250 -kyr ice core record. Nature, 364:218-220.

Delmas R J & Petit J R 1994 Present Antarctic aerosol composition: A memory of ice age atmospheric dust. Geophysical Research Letters 21:879-882.

Grootes P M, Struiver M, White J W C, Johnsen S & Jouzel J 1993 Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores. Nature 366:552-554.

Grousset F E, Biscaye P E, Revel M, Petit R-J, Pye K, Joussaume S & Jousel J 1992 Antarctic (Dome C) ice-core dust at 18 k.y. B.P.: Isotopic constraints on origins. Earth and Planetary Science Letters 111:175-182.

Hirao Y, Mabuchi H, Fukuda E, Tanaka H, Imamura T, Todoroki H, Kimura K & Matsumoto E 1986 Lead isotope ratios in Tokyo Bay sediments and their implications in the lead consumption of Japanese industries. Gechemical Journal 20:1-15.

Hong S, Candelone J P & Boutron C F (1994) Greenland ice evidence of hemispheric scale pollution for lead two millennia ago by Greek and Roman civilizations. Science 265:1841-1843.

Joussaume S 1993 Paleoclimatic tracers: An investigation using an atmospheric general circulation model under ice age conditions 1. Desert dust. Journal of Geophysical Research 98: 2767-2805.

McMichael A J, Baghurst P A, Wigg N R, Vimpani G V, Robertson E & Roberts R J 1988 Port Pirie cohort study: Environmental exposure to lead and children's abilities at the age of four years. New England Journal of Medicine 319:468-475.

Murozumi M, Chow T J & Patterson C C 1969 Chemical concentrations of pollutant aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata, Geochimica et Cosmochimica Acta 33:1247-1294.

Mushak P, Davis J M, Crocetti A F & Grant L D 1989 Prenatal and postnatal effects of low-level lead exposure: Integrated summary of a report to the U.S. Congress on childhood lead poisoning. Environmental Research 50:11-36.

Needleman H L 1991 Childhood lead poisoning: A disease for the history texts. American Journal of Public Health 81:685-687.

Ng A & Patterson C C 1981 Natural concentrations of lead in ancient Arctic and Antarctic ice. Geochimica et Cosmochimica Acta 45:2109-2121.

Nriagu J O 1983 Lead and Lead Poisoning in Antiquity. Environmental Science and Technology, John Wiley, New York.

Nriagu J O 1990 The rise and fall of leaded gasoline. Science of the Total Environment 92:13 - 28.

Patterson C C 1956 Age of meteorites and the earth. Geochimica et Cosmochimica Acta 10:230-237.

Patterson C C 1965 Contaminated natural environments of man. Archives for Environmental Health 11:344-360.

Patterson C C & Settle D M 1976 The reduction of orders of magnitude errors in lead analysis of biological materials and natural waters by controlling the extent and sources of industrial lead contamination introduced during sample collecting, handling and analysis. Proceedings of the Seventh Materials Research Symposium. US Government Printing Office, Washington DC. National Bureau of Standards Special Publication 422:321-351.

Rabin R 1989 Warnings unheeded: A history of child lead poisoning. American Journal of Public Health 79:1668-1674.

Ritsen P I, Esser B K, Niemeyer S & Flegal A R 1994 Lead isotopic determination of historical sources of lead to Lake Erie, North America. Geochimica et Cosmochimica Acta 58:3297-3305.

Richards T W & Lembert M E 1914 The atomic weight of lead of radioactive origin. Journal of the American Chemical Society 36:1329-1344.

Rosman K J R, Chisholm W, Boutron C F, Candelone J P & Gorlach U 1993 Isotopic evidence for the source of lead in Greenland snows since the late 1960s. Nature 362:333-335.

Rosman K J R, Chisholm W, Boutron C F, Candelone J P & Hong S 1994a Isotopic evidence to account for changes in the concentration of lead in Greenland snow between 1960 and 1988. Geochimica et Cosmochim. Acta 58:3265-3269.

Rosman K J R, Chisholm W, Boutron C F, Candelone J P & Patterson C C 1994b Anthropogenic lead isotopes in Antarctica. Geophysical Research Letters 21:2669-2672.

Rosman K J R, Chisholm W, Hong S, Boutron C F & Candelone J P 1995 Lead isotope record in ancient Greenland ice. Proceedings of 10th International Conference on Heavy Metals in the Environment, Hamburg. 1:34-36.

Rosman K J R, Loss R D & de Laeter J R 1984 The isotopic composition of tin. International Journal of Mass Spectrometry and Ion Physics 56:218-291.

Shen G T & Boyle E A 1987 Lead in Corals: reconstruction of historical industrial fluxes to the surface ocean. Earth and Planetary Science Letters 82:289-304.

Shirahato H, Elias R W & Patterson C C 1980 Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. Geochimica et Cosmochimica Acta 44:149-162.

Soddy F 1913 Radioactivity. Annual Report of the Chemical Society 105:1402-1408.

Tatsumoto M & Patterson C C 1963 Concentrations of common lead in some Atlantic and Mediterranean waters and in snow. Nature 199:350-352.

Wolff E W & Suttie E D 1994 Antarctic snow record of southern hemisphere lead pollution. Geophysical Research Letters 21:781-784.